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A handwritten signature in black ink, appearing to read "Theodore M. Gawlicki".

Theodore M. Gawlicki
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July 25, 2003

"Subscribed and sworn to before me
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A handwritten signature in black ink, appearing to read "Eugene J. Joseph Jr."
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RUSSIAN PATENT
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In response to No. of 6/11/2003

[stamp:]
FIIP
June 27, 2003
Department No. 04

Form No. 01IZ-2003

(74)

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(21) Our No. 2002120653/04(021637)
*In correspondence, please refer to the Application No.
and indicate the date you received this document.*

**DECISION TO GRANT
AN INVENTION PATENT**

(21) Application No. 2002120653/04(021637) (22) Application date: 7/29/2002

(24) Date of patent: 7/29/2002

(85) Date of international application based on the national phase:

PRIORITY HAS BEEN ESTABLISHED BY DATE:

(22) of application 7/29/2002
 (23) of submission of additional information of
to the previous application No. of
 (62) of priority of invention per original application No. of
from which this application was separated
 of filing the original application No. of
from which this application was separated
 (66) of filing the previous application No. of
 (30) of filing the first application in a member state of the Paris Convention
(31) No. of the first (32) Filing date of the first (33) Country Claim(s)
application(s) application(s) code

1.
2.
3.

(86) PCT application No. (96) EA Application No.

(87) No. and date of publication of the PCT application

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(indicate country code)

(51) IPC 7 C07C 409/10

(54) Name of invention: Method of Producing Cumene Hydroperoxide

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(see reverse)

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Form No. 01a

(21) 2002120653/04(021637)

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- CLAIMS -

(54)(57)

1. A method of producing cumene hydroperoxide by continuous aqueous-emulsion oxidation at a high temperature and pressure in a cascade of reactors in the presence of ammonia, *wherein* the process is conducted in the presence of a mixture of an aqueous solution of an ammonium salt (e.g. ammonium bicarbonate, ammonium carbonate, ammonium carbamate or a mixture thereof) with a concentration of 0.001 – 0.5 mass % and an aqueous solution of ammonia with a concentration of 0.001 – 0.5 mass %, which is fed into each oxidation reactor in an ammonia : ammonium salt mass ratio of 1:100 to 100:1.
2. A method according to Claim 1 *wherein* the process is conducted at a temperature of 100 – 120°C in the first reactor with a gradual decrease to 80 – 90°C in the last reactor and at a gage pressure of up to 5 atm.

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7 examples

US
(56) SU 5908962 A, 6/1/1999
RU 2183623 A, 7/1/1998
US 642305 A, 1/15/1979
US 5767322 A1, 7/1/1998
US 2632026 A, 3/17/1953

When publishing the patent-granting data, the applicant's description of the invention will be used taking into account the replacement pages 6, 8 and 10 submitted in the applicant's response dated 6/11/2003 and the additional example presented in the applicant's letter dated 9/26/2002.

Addendum:

1. Explanation of procedure for paying patent fees (1 sheet, 1 copy)
2. Summary edited by experts.

Chief state patent expert,
Department of Technology of
Organic Compounds

[signature] G.S.Mosina
240-34-93

IPC₆ C07C 407/00, 409/10

Method of Producing Cumene Hydroperoxide

This invention relates to the field of petrochemical synthesis, i.e. to the technology of oxidation of cumene by an oxygen-containing gas (usually by air oxygen) with formation of cumene hydroperoxide (CHP) whose subsequent decomposition in the presence of an acid affords phenol and acetone. The said transformations create the basis for industrial heavy-tonnage production.

Two primary methods of producing cumene hydroperoxide (CHP) are known.

The first, so-called "dry" method is when liquid phase oxidation of pure cumene is conducted in the presence of catalytic amounts of basic compounds, i.e.:

- carbonates of alkali and alkaline-earth metals [US Patent No. 2613227 (1952), US Patent No. 2619509 (1952), US Patent No. 2689936 (1954)],
- sodium bicarbonate [US Patent No. 2577768 (1951)],
- calcium hydroxide [US Patent No. 2632774 (1953)],
- barium oxide [US Patent No. 4153635 (1979)],
- substituted ammonium salts [US Patent No. 4192952 (1980) and other compounds that, in the process of oxidation, are suspended in cumene.

The use of such basic compounds relates to the following circumstances:

- In the process of oxidation of cumene, trace amounts of organic acids, particularly formic acid, are formed along with the target product, CHP, and two main impurities, acetophenone (ACP) and dimethylphenylcarbinol (DMPC).

The presence of formic acid in the cumene oxidation reaction mass inevitably leads to acid-catalytic decomposition of CHP with formation of phenol and acetone. It is known that phenol is a strong inhibitor of the free-radical oxidation of alkylaromatic hydrocarbons and cumene in particular. Thus, the presence of even trace amounts of formic acid significantly slows the oxidation process rate. Therefore, efforts are made to conduct the cumene oxidation reaction at pH ~ 5 - 7.

The most obvious technique for removing acids from the cumene oxidation reaction mass is to conduct this process in the presence of basic compounds.

The second, so-called "wet," aqueous-emulsion method of producing cumene hydroperoxide by oxidation of cumene consists of conducting the oxidation reaction in a three-phase system:

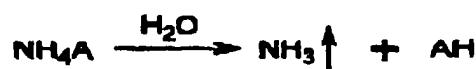
- organic phase consisting of cumene and the products of its oxidation,
- aqueous phase consisting of solutions of basic compounds,
- gaseous phase consisting of oxygen-containing gas (usually air).

Both the "dry" and the "wet" cumene oxidation methods are conducted in the presence of basic compounds.

Basic compounds dissolve in water much better than in hydrocarbons. Therefore, the mass transfer process in heterogeneous "organic phase - water" systems is much more effective than in "organic phase - solid dispersion" systems. So, in terms of the more complete and faster removal of acids from the system, the "wet" oxidation method should be recognized as more effective than the "dry" method.

This invention specifically relates to the "wet" method of cumene oxidation.

A method is known for producing CHP by oxidation of cumene by air at a high temperature. The oxidation reaction is conducted in the presence of ammonium salts of organic acids or carbonic acid; 0.05 - 50% aqueous solutions of the said salts are used. The said method (USSR Author's Certificate No. 567723, published on 9/9/77 in Bulletin of Inventions No. 29) has the following disadvantages, which we will first discuss using ammonium salts of organic acids as examples. Under high-temperature (80 - 120°C) conditions of the cumene oxidation process, partial thermal decomposition of the salts occurs by the following reaction:

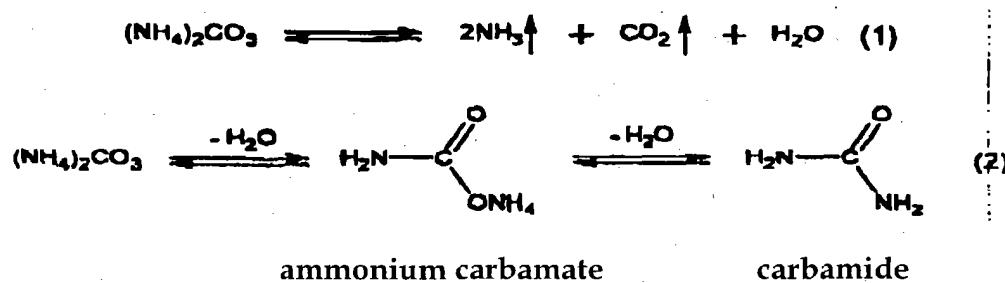


where: A is the symbol of an organic anion,

AH is the symbol of the acid of that organic anion.

Since ammonia features a significant volatility, the liquid phase predominantly contains the acid that inhibits the cumene oxidation process. Moreover, it is economically inefficient to use ammonium salts of such relatively expensive organic acids as ethylenediaminetetraacetic or 1,10-decanedicarbonic acid.

If ammonium carbonate, an ammonium salt of carbonic acid, is used, then under high-temperature conditions, decomposition of the said salt occurs according to the following reaction mechanisms:



Reaction (1) predominately occurs in the aqueous phase while reaction (2) dominates in the organic phase.

An increase in the temperature shifts the equilibrium in Reaction (1) to the right while a decrease in the temperature shifts it to the left. Industrial cumene oxidation reactors are equipped with condensation systems whose function is to condense the carryover vapors of cumene and, partially, of water. In the condensation process that is conducted under lower temperature conditions, the equilibrium in Reaction (1), as mentioned above, shifts to the left, which results in a partial recovery of the alkaline agent in the cumene oxidation reactor. That circumstance has a positive effect on the process performance. On the other hand, Reaction (2) eventually leads to

formation of carbamide (urea) whose aqueous solution has a much lower pH than the corresponding ammonia solutions. That circumstance inevitably leads to a worsening of the characteristics (rate and selectivity) of the oxidation process.

Furthermore, the said salts are practically insoluble in organic phases while the volume of the organic phase represents the larger part of the solution. That is why the salts clog the pipelines and precipitate on the walls of heat-exchanging equipment, which leads to reduced heat transfer coefficients. This circumstance especially impairs the process of CHP rectification/concentration that follows the cumene oxidation step.

As follows from the description of invention (Author's Certificate No. 567723), that process is essentially a "dry" oxidation process since the amounts of the aqueous solutions added are so small (e.g., 50% solutions of ammonium carbonate are used in an amount of 0.17 g per 300 g of cumene) that all water is dissolved.

A process is known for producing cumene hydroperoxide using air oxygen in the presence of gaseous ammonia in the amount of no less than 0.5% of the reacted oxygen [US Patent No. 2632026 (1953)]. Although the cumene conversion (up to 21%) and CHP formation selectivity (up to 97.3%) characteristics of that process are good, its primary disadvantage is a very low oxidation rate.

The said process has the following primary disadvantage: in feeding gaseous ammonia into the reactor, most of the ammonia escapes into the atmosphere. All existing CHP synthesis plants are equipped with waste-gas afterburning units (thermal afterburning units are used more often than the catalytic ones). This, in turn, leads to the presence of nitrogen oxides in the gaseous emissions and has a negative environmental impact. Furthermore, the patent's high conversion and selectivity characteristics are achieved at a very low cumene oxidation rate (0.6% cumene per hour). In its technical essence, the closest prototype of the proposed method is a process for producing cumene hydroperoxide by oxidation of cumene in an aqueous/alkaline emulsion at a temperature of 92 – 107.2°C and a gage pressure of 5 atm in a horizontal cascade of reactors (no fewer than two) in two steps: cumene sequentially passes the first-step and second-step reactors into each of which the oxidant (air) is fed. In order to neutralize the acids, an aqueous solution of sodium carbonate is fed into the second step of the process; in the course of neutralization, sodium carbonate is transformed into sodium bicarbonate. The aqueous salt solution from the second step of the process is treated by ammonia or ammonium hydroxide up to pH = 10.5 – 11.5; in the course of that process, sodium bicarbonate is transformed into the mixed salt, NH_4NaCO_3 . The neutralized solution is fed into the first-step reactors in a ratio of (3.5 – 2.6):1 to the cumene that is fed for oxidation [US Patent No. 5767322, 1998: prototype].

US Patent No. 5908972, 1999, held by the same applicant, proposes, under the conditions similar to US Patent No. 5767322, feeding ammonia in an amount at least stoichiometric in relation to the amount of acids formed in the

cumene oxidation process while monitoring the salts thus formed under ambient pH of 10.0 – 12.0 while ammonia is injected directly into the first-step reactors.

It is known that, in oxidation of cumene, two byproducts, dimethylphenylcarbinol (DMPC) and acetophenone (ACP), are formed along with CHP; the amount of those byproducts determines, ultimately, the yield of commercial products and the mass of the undesirable production waste, the phenolic resin; it also complicates the process of producing commercial products of the required quality. Therefore, an improvement of the cumene oxidation selectivity at a sufficiently high conversion (optimal CHP concentration in the flow leaving the oxidation unit is 25 – 30%) is an important issue for increasing the effectiveness of the industrial technology.

The following disadvantages of the prototype process can also be indicated:

- using different neutralizing solutions for the first and second oxidation steps, which complicates the technological scheme;
- the presence of sodium salts, which can precipitate on the walls of heat-exchanging equipment;
- leads to reduced heat transfer coefficients;
- furthermore, the large amount of the neutralizing aqueous solution in relation to the cumene that is being oxidized, (3.5 – 2.6):1. Providing for a required capacity of the oxidation plant results in larger reactor volumes compared to the "dry" oxidation method.

The aim of this invention is to simplify the technology while maintaining the high selectivity and rate of cumene oxidation without impairing the environmental characteristics of the process.

The said aim is achieved when the process of continuous aqueous-emulsion oxidation of cumene is conducted in a cascade of flow-through reactors by bubbling air through a water-cumene emulsion. The process is conducted at a temperature of 120°C in the first reactor, lowering it to 80°C in the last reactor, and at a gage pressure of 5 atm, in the presence of a mixture consisting of a 0.007 - 0.5% aqueous solution of ammonia and a 0.001 - 0.5 mass % solution of an ammonium salt (ammonium bicarbonate, ammonium carbonate, ammonium carbamate or a mixture thereof). The ammonia: ammonium salt mass ratio is (1:100) : (100:1), preferably (1:10) : (10:1). The oxidative feedstock is fed into the bottom part of each reactor while the aqueous phase is fed into the top part of each reactor. The organic layer of the reaction mass gravity overflows into a vessel, from which it is periodically discharged. The aqueous phase is periodically discharged from the bottom of the reactor and flows through valves into a vessel. The gaseous phase is partially condensed in a cooler, passes an activated-coal filter, where partial sorption of cumene takes place, and then goes, through control valves, into an oxygen analyzer and rheometer. The discharge rates of the liquid phases are controlled by pumps. The reactor temperature is set by a thermostat (oil is used as a heat-carrying agent) and measured by a thermocouple.

An essential distinctive feature of the proposed aqueous-emulsion process of cumene oxidation is that the process is conducted using a mixture

consisting of a 0.001 - 0.5 mass % aqueous solution of ammonia and a 0.001 - 0.5 mass % solution of an ammonium salt (ammonium bicarbonate, ammonium carbonate, ammonium carbamate or a mixture thereof) at an ammonia: ammonium salt mass ratio of (1:100) : (100:1), preferably (1:10) : (10:1).

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makes it possible to substantially simplify the process technology, at a process selectivity of ~94% or better and a conversion of 23%, by excluding the use of neutralizing agents that form solid deposits on heat-exchanging equipment.

The industrial applicability of the proposed method is confirmed by the following examples.

EXAMPLES 1 - 6.

The basic experiment parameters (a pressure of 5 atm and a temperature of 80 - 120°C) simulate the working conditions of the individual reactors of an actual industrial plant. The feedstock flow rate was selected in such a manner that the CHP concentration gain corresponded to a six-reactor system.

In the experiments, cumene of a purity of no less than 99.85% was used. The aqueous phase was prepared from ammonium bicarbonate of the "chemically pure" grade with an ammonia content of no less than 21.7%.

The oxidative feedstock for each of the experiments was either pure commercial cumene (first reactor, $T = 120^{\circ}\text{C}$) or oxidation products obtained in the course of the previous experiments.

The concentration of CHP was determined by iodometric titration.

The concentrations of ACP and DMPC were determined by gas-liquid chromatography: a chromatograph with a flame ionization detector and a 25 m long column with an outer diameter of 0.32 mm; stationary liquid phase: OV-1; $T_{\text{initial}} = 50^{\circ}\text{C}$, temperature rising rate: $8^{\circ}\text{C}/\text{min}$, $T_{\text{final}} = 20^{\circ}\text{C}$. The quantitative calculations were performed using n-pentadecane as the internal standard.

The aqueous phase flowrate was 6 - 7 ml/hr while the oxidative feedstock flowrate was 200 - 260 ml/hr.

In order to simulate the operation of an actual six-reactor industrial plant, temperatures falling into the range of 120 - 87.8°C were selected (see Table 1). For the first reactor ($T = 120^{\circ}\text{C}$), pure commercial cumene ($C_{\text{CHP},0} = 0.07\%$) was used as the oxidative feedstock. In the subsequent experiments, the products obtained in the course of the previous experiment were used as feedstock.

The experiment was conducted as follows. In the atmosphere of nitrogen, the reactor was filled, until liquid overflowed into the vessel, with the oxidative feedstock and 20 ml of the 0.001-0.5 mass % aqueous solution of the ammonium salt and the reactor heating was turned on. After the required temperature was reached, the nitrogen flow was stopped and air feeding was started. In 1 hour, the first sample of the organic phase was taken through a siphon tube and analyzed for CHP content. In another hour, the second

sample was taken and sampling was done in that manner until the expected CHP concentration was reached. After that, the pumps were turned on and in 12 - 15 hours the steady mode was established. The aqueous phase was periodically (every 0.5 hours) discharged from the bottom of the reactor. The organic phase was continuously overflowing into a receiving vessel that was discharged periodically. After a steady mode was reached, organic phase samples were taken every 3 - 4 hours and analyzed for the content of CHP (titration) as well as the contents of DMPC and ACP (gas-liquid chromatography). The duration of each experiment was 24 to 72 hours.

The ammonium salt concentration for each of the experiments was selected experimentally. It has been found that, for each of the simulated reactors, there exists an optimal concentration below which the oxidation reaction rate falls significantly while, at higher concentrations, a decrease in selectivity is observed.

The data thus obtained are shown in Table 1.

T°C	Concentration, mass %		C _{CHP,0} , %	C _{CHP} , %	Cumene conversion, %	Selectivity of CHP formation, %	pH of aqueous phase	pH of org. phase
	Ammonium salt	Ammonia						
120.0	0.001	0.005	10.07	6.41	5.23	95.6	6.7	6.2
102.0	0.005	0.007	6.41	11.62	5.01	95.0	6.9	6.3
98.0	0.015	0.005	11.62	17.63	4.76	94.7	7.0	6.9
94.4	0.03	0.05	17.63	22.20	3.80	94.0	7.3	6.4
91.0	0.08	0.02	22.20	24.75	2.48	92.7	7.2	6.3
80.0	0.04	0.08	24.75	28.8	3.40	92.5	7.3	6.3

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Example 7

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The process is conducted similarly to examples 1 - 6 but, in oxidation, an aqueous solution of an ammonium salt obtained by passing carbon dioxide gas through an aqueous solution of ammonia is used. At an oxidation temperature of 120°C and a pressure of 5 atm, the conversion is 5.3% and the selectivity is 85.7%.

[handwritten:] CO₂ Gas

INVENTION CLAIMS

"A method of producing cumene hydroperoxide by continuous aqueous-emulsion oxidation at a high temperature and pressure in a cascade of reactors in the presence of ammonia, wherein the process is conducted in the presence of a mixture of an aqueous solution of an ammonium salt (e.g. ammonium bicarbonate, ammonium carbonate, ammonium carbamate or a mixture thereof) with a concentration of 0.001 - 0.5 mass % and an aqueous solution of ammonia with a concentration of 0.001 - 0.5 mass %, which is fed into each oxidation reactor in an ammonia : ammonium salt mass ratio of 1:100 to 100:1."

2. A method according to Claim 1 wherein the process is conducted at a temperature of 100 - 120°C in the first reactor with a gradual decrease to 80 - 90°C in the last reactor and at a gage pressure of up to 5 atm.